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SULFUR STUDIES WITH SOME CHERNOZEMIC SOILS

by



PIRMPOON RATANALERT

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "Sulfur Studies with Some Chernozemic Soils" submitted by Pirmpoon Ratanalert, B. Sc., in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

Routine tests for available S by the ASFTL on soil samples submitted by farmers in the fall of 1970 from East Central Alberta found low levels of S in some Chernozemic soils of the Wainwright-Vermilion region. Sulfur deficiency in that area had not been anticipated nor expected. As a consequence, experiments were conducted: to determine by field experiments the S responses, if any, of crops grown on some Chernozemic soils of the Wainwright-Vermilion region which were low in water soluble SO_4 -S content; to compare those results with ones from the same or similar soils in greenhouse experiments under controlled conditions; and to investigate the effect of S fertilization on composition of the plants from those experiments.

Field plot experiments were conducted in the Wainwright-Vermilion region and, for comparison purposes, on two Luvisols known to be S deficient. Field experiments were carried out at seven locations employing alfalfa, barley and rape as test crops with fertilizer treatments of nil, NPK and NPKS. Significant yield increases from S fertilization were obtained with rape at two locations and with barley at one location among the five field experiments on Chernozemic soils. In the field experiments rape appeared to be the crop most sensitive to S deficiency. Chemical analyses on plant materials from the field experiments found that the fertilization treatments produced some differences in plant composition.

The first greenhouse experiment included Chernozemic soils having various levels of available S and, for comparison, two Luvisolic soils. Barley was the test crop. Yield responses to S were obtained with all soils except ones with high test values for available S. In that experiment the effects of S application on yields and plant composition were related to the available S status of the soils. Fertilization with NPK of soils of low sulfur status reduced grain yield below the yield of grain on the nil treatment although the vegetative growth was considerably increased by that fertilization.

A second greenhouse experiment was conducted with the objective of confirming that NPK fertilization of soils of low S status adversely affects yield of barley grain. Because of experimental difficulties, the results of the second greenhouse experiment were not very conclusive but effects of the fertilizer treatments on plant composition were similar to those obtained from the previous experiments.

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INTRODUCTION

Sulfur (S) plays an important role in living processes. It is needed for synthesis of the amino acids methionine, cystine, and cysteine which are components of proteins. Sulfur is also a constituent of the vitamins biotin and thiamine, of the respiratory compound coenzyme A, and of glutathione. Sulfur compounds have a role in the elaboration of oil in crops such as flax, soybeans, and rape. It has been shown that the S level in crops affects cold resistance of plants in some cases. Thus, S is necessary for both plants and animals.

Plants obtain most of their S in the form of the sulfate ion taken up from the soil. Sulfur dioxide (SO_2) in the atmosphere can also be absorbed by plant leaves even though the quantities obtained in that way are normally very small. Sulfate-sulfur ($\text{SO}_4\text{-S}$) for plant uptake comes primarily from the mineralization of organic S or from the weathering of minerals such as sulfides, both resulting in soluble sulfate in the soil solution. Small amounts of S compounds are brought down in precipitation. Most of the S in humid region soils is in organic form whereas in arid areas the sulfate ion is often present in the soil solution as an anion accompanying such common cations as calcium, magnesium, potassium, and sodium. However, in some soils $\text{SO}_4\text{-S}$ is adsorbed on 1:1 clays or the hydrous oxides of iron and aluminum.

It has been known since 1936 that S deficiency affects some crops in parts of Alberta (Newton, 1936). That was first proven at the Breton Plots which were established on a Gray Luvisol near the town

of Breton in 1929. The Breton Plots were started in an endeavor to explain, and improve, the low productivity of such soils in that district. Initially it was thought that Gray Luvisols in the region west and southwest of Edmonton were generally S deficient if leguminous crops were grown on them. However, not all Alberta Gray Luvisols and Dark Gray Luvisols have been found to be S deficient (Walker, 1959; Sorensen, 1965). In spite of that, for a period of 30 to 35 years following the initial identification of S deficiency in Alberta, soils identified as S deficient were almost exclusively strongly leached ones of rather low organic matter content. The possibility of some Chernozemic soils being S deficient had not been seriously considered; those soils have a high organic matter content and precipitation where they occur tends to be somewhat lower than it is in most Luvisolic regions of the province. The presence of considerable quantities of water soluble sulfate salts in parts of the Chernozemic soil regions of Alberta also contributed to the expectation that S deficiency was unlikely there.

It has been very difficult to identify S deficient soils by soil testing methods only. The S requirement of common crops ranges from about 5 - 35 kg/ha. Because of the small quantity of S required by crops, satisfactory soil test methods for routine use in soil testing laboratories were not available for many years. For that reason lack of a practical soil test procedure for determining available S has long hampered agricultural production. Field experiments and visual identification of deficiency symptoms were the principal ways of determining needs for S fertilization. Recently, however, a soil test method for available S determination in farm soils has been described (Carson et al.,

1972). That method has been used by the Alberta Soil and Feed Testing Laboratory (ASFTL) since 1970. Amounts of "available sulfate-sulfur" ($\text{SO}_4\text{-S}$) as low as 1 ppm or less of S can be detected by the method. Based on the ranges of $\text{SO}_4\text{-S}$ found in farm soils, the ASFTL classifies soils into three categories. Soils with less than 3 ppm of $\text{SO}_4\text{-S}$ are likely to show S deficiency when cropped; soils testing above 5 ppm $\text{SO}_4\text{-S}$ are not likely to respond to S application; and soils with levels between 3 and 5 ppm $\text{SO}_4\text{-S}$ are considered borderline in their content of available S.

Routine testing for available S in farm samples from East Central Alberta was commenced in 1970 as a part of a general survey being conducted by the ASFTL. It was found that some of the soil samples received from farmers in the Wainwright - Vermilion region were low in available S. That surprising result led to the investigations on S status of soils in the Wainwright - Vermilion region reported in this thesis.

Thus, the objectives of this investigation were: to determine by field experiments the S responses, if any, of crops grown on some Chernozemic soils of the Wainwright - Vermilion region which were low in water soluble S content; to compare those results with ones from the same or similar soils in greenhouse experiments under controlled conditions; and to investigate the effect of S fertilization on composition of the plants in those experiments.

REVIEW OF LITERATURE

Role of Sulfur in Plants and Animals

Sulfur has been recognized as one of the essential elements for plant growth for approximately 130 years (Beaton and Fox, 1971). It has several important roles and forms in plants and organisms (Tisdale and Nelson, 1967). The forms of S taken up by plants and animals are somewhat different. Plants obtain most of their S requirement in the form of the sulfate ion (SO_4^{--}) from soils. Under special circumstances, such as in some industrial areas, SO_2 is present in the atmosphere in substantial quantities (Walker, 1969; Walsh and Hoeft, 1970) and an appreciable amount is absorbed through plant leaves (Burns, 1967; Hoeft et al., 1972). Sulfur, whether taken in by plants as SO_4^{--} or SO_2 , can be reduced in plants and is then used for structural and metabolic purposes. Animals (and humans), except ruminants, can not utilize inorganic S; they must be supplied with the S-containing amino acids methionine and cystine as well as the S-bearing vitamins biotin and thiamine. Ruminants can utilize sulfate, sulfide, and to a lesser extent elemental S, because of the synthesis of S-containing amino acids from such materials through the activity of microorganisms in the rumen (Allaway and Thompson, 1966; Tisdale and Nelson, 1967). Microorganisms can assimilate either organic or inorganic forms of S (Allaway and Thompson, 1966). Organic forms of S, for example methionine and cystine, and inorganic forms such as $\text{SO}_4\text{-S}$, hydrogen sulfide, and elemental S,

can be assimilated by various microorganisms found in soils.

Sulfur absorbed by plants is synthesized into organic compounds which form part of the structural framework of plants or play a role in plant metabolic processes (Salisbury and Ross, 1969). Sulfur is required for the formation of the amino acids, cystine, cysteine, and methionine which are incorporated into proteins. In most plants, methionine and cystine account for about 90 percent of the total S (Allaway and Thompson, 1966). Sulfur is also needed for the synthesis of the vitamins biotin and thiamin (or vitamin B₁), glutathione, and of coenzyme A (Beaton and Fox, 1971; Tisdale and Nelson, 1967). Plants of the mustard and onion families need S for the formation of the glucoside oils. Sulfur is required for the formation of ferredoxin which has an important role in all photosynthetic processes (Beaton and Fox, 1971). The formation of disulfide linkages (-S-S-) are associated with the composition of protoplasm, and the quantity of sulfhydryl groups (-SH) in plant tissues has been shown to be related to increased cold and drought resistance in some species (Tisdale and Nelson, 1967). Sulfur is involved in the formation of chlorophyll, even though S does not constitute a part of this substance (Beaton and Fox, 1971). Sulfur is also required for the activation of certain proteolytic enzymes such as the papainases (Beaton and Fox, 1971; Tisdale and Nelson, 1967). Some microorganisms, for example green S bacteria and purple S bacteria, use S in the form of H₂S (sulfide) instead of water as an exogenous electron donor for the synthesis of cell material from CO₂ (Stanier et al., 1963).

This brief review shows that S is vital to animals, plants, and microorganisms, and that there are several forms of S in living tissues with a variety of functions.

Effects of Sulfur Deficiency and Sulfur Fertilization on Plants and Soils

Sulfur fertilization of soils deficient in that plant nutrient has been practised extensively in order to obtain improved yields which are often accompanied by better quality of the plant products concerned. When plants lack adequate amounts of available sulfur, a variety of visible and chemical effects have been reported.

Sulfur deficient plants are often pale green in color. Meyer et al. (1960) and Beaton et al. (1971) have reported that S deficient plants are chlorotic because S deficiency adversely affects chlorophyll formation.

Sulfur deficiency affects metabolism of nitrogen (N) when there are adequate amounts of N in available form. Reduced protein synthesis, accumulation of organic N compounds such as amino acids, and accumulation of such inorganic materials as nitrate and ammonia have been reported to result from S deficiency (Beaton, 1966; Coleman, 1957; Nightingale et al., 1932). It has also been reported that reduction of nitrates and oxidation of sugars are slowed even though not entirely inhibited when S is deficient. That results in accumulation of carbohydrates and nitrates in the S deficient plants (Meyer et al., 1960; Nightingale et al., 1932). Thus, S deficiency may cause higher than normal levels of non-protein and total N in affected plants (Anderson and Spencer, 1950). Numerous other workers have reported results revealing a variety of effects on N metabolism when S deficiency has affected different crops (Beaton, 1966; Rendig and Oputa, 1970).

Sulfur fertilization has often been reported to affect the composition and health of plants. Sulfur application to wheat grown on a S deficient soil improved the nutritive value (Bentley et al., 1960). The content of methionine, cystine, and percent S in several crops has been increased by S application (Beaton and Fox, 1971; Renner et al., 1953; Caldwell et al., 1972; Tisdale and Nelson, 1967). Other effects of S fertilization on plant composition include increased contents of crude protein, vitamin A, oil content, and quality of oil-seed crops, as well as better color of vegetables, turf grass and Douglas fir plantations. Beaton and Fox (1971) have reported that S fertilization helps maintain and prolong stands of alfalfa and red clover, and that it sometimes increases drought and disease tolerance.

The N:S ratio in crops is an aspect of plant sulfur nutrition which has been studied frequently. Many workers (Beaton et al., 1971; Caldwell et al., 1972; Ensminger and Freney, 1966; Martin and Walker, 1966) have suggested that this ratio is a useful index of the nutritive value of feeds and an indication of sulfur availability in soils. Generally, an N:S ratio of from 14 to 16 to one (Beaton and Fox, 1971) or less than 15 to one (Jones et al., 1972) has been considered adequate for good plant growth. Coleman (1966) has suggested N:S ratios of 15 to 20 to one are satisfactory for ruminant feeds. However, a narrower N:S ratio in forages, not greater than 10:1, has been suggested as desirable for ruminants because they utilize N in feeds more efficiently than monogastric animals. Allaway and Thompson (1966) suggested that the N:S ratio found satisfactory for optimum plant growth might not be satisfactory for ruminant feeds. The N:S ratio in plants can be changed

by S fertilization, especially of S deficient soils. Beaton and Fox (1971) have reported that the N:S ratio in a number of alfalfa and red clover materials was reduced from 18 to 13 by S fertilization and they include a table that reports the N:S ratio of alfalfa forage was reduced from 42 to 15 by application of 26 ppm S. In a greenhouse experiment reported by Jones et al. (1972) N:S ratios ranged from 15 to 80 in ryegrass depending on the S status of the soils on which the plants grew.

The maturity of plants is often hastened by S fertilization. It was reported (Beaton et al., 1971) that corn grown in Nebraska receiving S fertilizer was mature before that receiving no S. In Minnesota, the moisture content of corn receiving S was lower than that of corn receiving no S. Even where S had little effect on yield of barley and oats in Alberta, maturity was 5 to 10 days earlier with S fertilization (Nyborg and Bentley, 1971).

Sulfur has been shown to have interactions with other nutrient elements. Fertilization with N plus S doubled yield of barley and increased yield of oats and rapeseed (Nyborg, 1968; Nyborg and Bentley, 1971). Carotene content of alfalfa hay in Nebraska was increased as a function of fertilization with P and S (Beaton et al., 1971). Olson and Engelstad (1972) suggest that the joint application of S and P does not give as much beneficial effect in acid soils of the humid tropics as on the neutral to alkaline soils in temperate regions. They suggest, however, that the two nutrients may have complementary effects when applied to tropical soils deficient in both. There have been reports of Mg having a highly positive interaction with S, increasing grain

yield of corn (Soofi and Fuehring, 1964).

Sometimes S fertilization has affected soil properties and reactions. Many workers (Caldwell et al., 1972; Hassan and Olson, 1966; McMahon et al., 1970) have shown that reduction of soil pH has resulted from S fertilizer applications. Carbonate content in soil has been decreased by S fertilization too (McMahon et al., 1970). Under conditions where there was slow decomposition of organic matter, it has been reported that S application increased the rate of crop residue decomposition on some soils (Beaton et al., 1971). In Alberta pollution with S or SO₂ from plants extracting elemental S results in about one-third of a million tons of S per year being released to the atmosphere or the environs. Since most of that SO₂ returns to earth in precipitation, and primarily in the vicinity of the emitting plants, it undoubtedly has an acidifying effect on soils there (Summers and Hitchon, 1971). Nyborg¹ has found that elemental S from some processing plants in Alberta has rendered small areas of soil close to those plants very acid.

This review has established that S deficiencies often affect the quality and composition of crops as well as their yields. Sulfur fertilization not only affects plants but also affects soil properties, especially if heavy rates of S are applied.

Forms of Sulfur in Soils

Sulfur occurs in soils in inorganic and organic forms. The earth's crust contains about 0.06 percent S, mainly in the form of

¹ Personal communication.

sulfides of metals such as the iron sulfide minerals (Bear, 1965; Tisdale and Nelson, 1967). Upon exposure to oxygen and weathering many sulfides are oxidized with the formation of sulfate. Autotrophic microorganisms are active in such oxidation, especially the genus *Thiobacillus* which is considered to be the most important S-oxidizing organism in soils (Burns, 1967). In other parts of the S cycle sulfate used by microorganisms, plants or animals is reduced and incorporated into their tissues in organic forms. Such S may be released as sulfate or as hydrogen sulfide when decomposition of organic matter occurs. Moorman (1963) has reported that under anaerobic conditions sulfates from the sea may accumulate as sulfides, mainly iron-polysulfides, in brackish or saline fine textured sediments which are high in organic matter. Subsequently, such iron sulfides may be oxidized and hydrolyzed, in the absence of calcium carbonate, to result in the formation of yellow colored ferric sulfate and sulfuric acid, thereby producing very acidic soils known as "cat-clays".

The amount and form of S in soils are often affected by climate. In the semiarid and arid regions, S is found primarily as sulfate salts of Ca, Na, K, and Fe, often being in the subsoil (Bear, 1965; Berger, 1972). In places there are very large amounts of such sulfate salts in soils. In some cases sulfate salts in the subsoil may be a significant source of S for plants (Harward and Reisenauer, 1966). Freney and Stevenson (1966) have reported that on the basis of C:N:S ratios found in many different regions most of the S in the surface horizons of soils of the humid and semiarid regions of the world is in the organic form. There is considerable variation in the C:N:S ratio of individual

soils, but the mean ratios for the soils from different regions of the world are remarkably similar (Freney and Stevenson, 1966).

The exact nature of organic S compounds in soils is not very definitely known (Freney and Stevenson, 1966). Freney (1967) mentions a number of procedures that have been employed by various workers for separating organic S-containing compounds. Hydriodic acid reducible S and carbon bonded S forms seem to be two main groups which have been separated by chemical extraction. Freney and Stevenson (1966) have reported that a significant fraction of the total S in soil, ranging from 24 to 77 percent, could be reduced to hydrogen sulfide with hydriodic acid, or hydrolyzed to inorganic sulfate by acid or alkali treatments. Such S is believed to be, at least in part, in the form of organic sulfate such as sulfate esters of carbohydrates and lipids. Another form of S is considered to be bonded to carbon as in cystine and methionine (Lowe, 1964; Lowe and de Long, 1963). Those workers have reported that of the total S from 12 to 58 percent was accounted for as carbon bonded S in some Quebec soils. However, only 17 to 26 percent of total S was accounted for as carbon bonded S in some Chernozemic and Podzolic soils of Alberta (Lowe, 1965). He also reported that from 33 to 63 percent of total S in those soils was accounted for as hydriodic acid reducible S. Those results reveal that there may be substantial differences in the proportions of the various forms of organic soil S in different soil Orders.

Various S-containing materials have been reported as being adsorbed on soil components. Sulfate can be adsorbed by clay minerals, especially 1:1 type clays, as well as by iron and aluminum hydroxides

(Tisdale and Nelson, 1967; Chao et al., 1964). Sulfate may also be bound covalently to organic fractions as sulfate polysaccharides or sulfate esters of phenols (Freney et al., 1962). Most S-containing amino acids in soils appear to be bound to the clay and humus fractions (Freney and Stevenson, 1966).

Thus, S forms in soils vary with types of pedogenesis and related factors such as parent materials, climate, biota, and soil management history.

Determining Need for S Fertilization

For purposes of this review the methods of trying to determine the need for S fertilization of crops may be classified under the four headings which follow.

Visible Deficiency Symptoms

Many crops show characteristic symptoms of S deficiency and that method may be used to identify soils deficient in available S for crop production. As mentioned before, chlorosis is a characteristic sign of S deficiency in crops. If that symptom is evident and recognized in the early stages of crop growth, fertilization may be practical to benefit the crop concerned.

Soil Analysis

A variety of chemical soil analyses have been tried and/or used to identify S deficient soils.

Total S of soils was found not to be related to the amount of S available to plants (Bentley et al., 1955; Williams and Steinbergs, 1964).

Various extractants and analyses have been employed in endeavors to remove the so-called "available S" for plants. Extraction of adsorbed sulfate has been tried as a means of determining the S supplying power or S status of soils. Many workers (Fox et al., 1964; Jones et al., 1972; Spencer and Freney, 1960) have used phosphate solutions as the extractant for adsorbed sulfate. They have obtained high correlations between phosphate extractable sulfate and plant growth or S uptake. However, Walker (1972) has reported that a phosphate solution did not give a better result than a water or a calcium chloride (CaCl_2) solution on soils of Alberta. Extractions aimed at removing soluble sulfate plus a fraction of organic S have been tried by many workers (Bardsley and Kilmer, 1963; Fox et al., 1964; McClung et al., 1959; Spencer and Freney, 1960; Williams and Steinbergs, 1959 and 1964). However, most of those methods did not give consistent correlations with plant growth or S uptake.

Carson et al. (1972) and Walker (1972) have been using 0.1 M CaCl_2 as the extractant to remove water soluble sulfate for purposes of determining the available S level of Alberta soils. Barrow (1961) has also reported that 0.15 percent CaCl_2 solution seems to give a good indication of available S. However, an 0.01 M CaCl_2 extracting solution used by Jones et al. (1972) did not give a good correlation of available S with S content of plants grown in a greenhouse experiment on some soils of England and Wales. Water alone is another soil

extractant used by many workers. Fox et al. (1964) received good correlations between available S determined that way and S uptake by plants. However, in some other cases, water extractable sulfate did not give a good correlation with S taken up by plants (Spencer and Freney, 1960). Reisenauer (1967) has stated that water as an extractant gave the same amount of extractable sulfate as a LiCl solution and determinations made with that extractant were well correlated with plant growth. Walker (1972) has also reported that water extraction gave the same result as CaCl_2 extraction. However, he suggested that CaCl_2 as an extractant has an advantage over water as the CaCl_2 facilitates filtration but does not affect the amount of S extracted. Therefore, a CaCl_2 solution is now used as the extractant for S in the Alberta Soil and Feed Testing Laboratory (ASFTL) in routine analysis (Carson et al., 1972).

This review leads to the conclusion that the effectiveness of various extractants for determining "available sulfur" may vary with the soil characteristics and properties. Fox et al. (1964) reported that on unweathered soils, water and phosphate extractants gave the best correlation with S taken up by plants whereas on weathered soils, water is an inefficient extractant. Under Alberta conditions a CaCl_2 solution is a favored extractant on the basis of present knowledge. That procedure, as described by Carson et al. (1972) is referred to as "the ASFTL procedure" in this thesis.

Plant Analysis

The S content of plants is another method which has been tried for detection of S deficiency. Separation of many different fractions

of S in plant materials has been involved in such research.

Total S is an obvious plant analysis to make in trying to identify S deficiency. There are numerous reports of such analyses, some of which show fairly good correlation with S deficiency for various crops. There are such reports: for alfalfa by Bentley et al. (1956), Cairns and Carson (1961), Caldwell et al. (1972), and Rendig (1956); for grain crops by Bentley et al. (1955); for perennial ryegrass by Cowling and Jones (1970) and Jones et al. (1972); and for soybeans, alfalfa, oats, barley, wheat, corn, and potatoes by Caldwell et al. (1972). However, total S determination on plant materials has not become a practical method of determining the need for S fertilization.

The $\text{SO}_4\text{-S}$ fraction of some legumes has been shown to be related to the S status of soils by Walker and Bentley (1961), Cairns and Carson (1961), Jones (1962), and Jones and Martin (1964). Other workers, Ulrich et al. (1959) for sugar beets, Lott et al. (1960) for coffee, and Benson et al. (1963) for apples, pears, and peaches, have shown similar relations for those crops. However, this method of determining S deficient soils has not had practical application.

As N and S are absorbed and incorporated into protein, the ratio of N to S has also been used as a means of identifying S deficient plants. There have been reports on the relationship between N:S ratio and the S status of soils: for perennial ryegrass by Cowling and Jones (1970) and Dijkshoorn et al. (1960), and Jones et al. (1972); for sugarcane by Gosnell and Long (1969); and for alfalfa, red clover, oats, and corn by Caldwell et al. (1972). Because of the recency of some of that work it is too early to know whether that approach will be used practically.

The lack of success in finding types of plant analyses for S which are suitable for practical identification of S deficient soils is understandable. The S content of plants is not entirely dependent on S in soils. Hoeft et al. (1972) report that alfalfa can take up SO_2 from the air through its leaves and they found up to 73 percent of the S in plants was taken from the atmosphere in a greenhouse experiment. Moreover, the S content in plants varies with both stage of growth and parts of plants analyzed. Thomas et al. (1944) reported that in the early stages of growth radioactive S accumulated in the leaves of barley and wheat temporarily, but later the concentration there steadily decreased. At the time of grain development, the organic S of the leaves was converted to sulfate and translocated to the grain where it was recombined in organic compounds. From 60 to 80 percent of the radioactive S was translocated to the barley and wheat grain during ripening. Harrison et al. (1944) reported that radioactive S accumulated in the kernels of spring wheat much more than in any other part of the plant. It has been reported that the N:S ratio of corn grain was higher than that of the sixth leaf at silking (Caldwell et al., 1972).

So far, routine identification of S deficient soils by plant analyses has not been practical.

Biological Tests

Biological methods employing microorganisms or plants have also been used to detect S deficiency or to assess the effect of S fertilization. Although a good correlation between growth of the microorganism, genus *Aspergillus*, and S status of soils has been obtained by

many workers (Picci, 1952; Spencer et al., 1964; and Spencer and Freney, 1960), it is not a method now used in routine soil testing.

Incubation methods have been attempted for determination of the S status of soils by many workers (Barrow, 1967; Cairns and Richer, 1960; Freney et al., 1962; Haque and Walmsley, 1972; and Williams, 1967), but those procedures have not found useful correlations. Therefore, use of plants on soils being tested is the oldest and most reliable method of determining the need for S fertilization.

Plant growth in the field and/or greenhouse has been used extensively for determination of S supplying power of soils. In field experiments, barley, oats, wheat, corn, rapeseed, red clover, alsike clover, and alfalfa were used as test crops in experiments reported by Bentley et al. (1955), Newton (1936), Nyborg (1968), Nyborg and Bentley (1971), Soofi and Fuehring (1964), Walker and Bentley (1961), Wyatt (1945), and many others. In greenhouse experiments, perennial ryegrass, rapeseed, alfalfa, wheat, oats, ground nuts, red clover, and turnips have been used by Chopra and Kanwar (1966), Cowling and Jones (1970), Jones et al. (1972), Nyborg (1964, 1968), Sanford and Lancaster (1962), and Tisdale et al. (1950). Coffee was used both in the greenhouse and in the field by Lott et al. (1960). These listings merely mention a few reported results.

Plants have also been used in two other types of research related to S supplying power of soils. The "A" and "a" values have been used to determine the S status of soils with radioactive S by many workers (Fox et al., 1964; Harward et al., 1962; Kamprath et al., 1957; Kilmer and Nearpass, 1960; Nearpass et al., 1961; Pawluk and Bentley, 1964). Greenhouse experiments have also been used to measure SO₂ uptake: by

alfalfa (Hoeft et al., 1972); by sunflower, corn, tobacco, and radish (Faller et al., 1970); and by wheat (Burns, 1967). However, those investigations have been more of a fundamental than an applied nature.

This review of research related to methods suitable for the practical identification of S deficient soils leads to two conclusions. Of the many laboratory methods which have been tried, the procedure based on the extraction of readily available sulfate with 0.1 M CaCl_2 solution appears best suited to Alberta conditions (Carson et al., 1972; Walker, 1972). However, that soil test procedure has not yet been established to be of very high reliability, and so field fertilizer experiments are still necessary to positively identify S deficient soils.

Occurrence of Sulfur Deficiency

Sulfur deficiency has been recognized in many regions of the world.

In tropical areas, S availability is somewhat variable, depending on such factors as: organic matter content of surface soils; texture; previous management of the soil; and amount of rainfall (Olson and Engelstad, 1972). It is therefore not surprising that S responses have been obtained in many tropical countries of Asia, Africa, and of Latin America for several economic crops such as rice, corn, sorghum, peanuts, oilpalm, sugarcane, cotton, jute, bananas, etc. (Beaton and Fox, 1971). A recent publication forecasts that as crop production is expanded and intensified in the tropics, especially when accompanied by applications of high analysis nitrogen and phosphorus fertilizers, S deficiency there will be a more frequent problem (Engelstad, 1972;

Olson and Engclstad, 1972).

Although S was described as "a nutrient slighted in agricultural research" (Alway, 1940), its deficiency in temperate region soils is long known and extensive. Beaton and Fox (1971) have reported that S response occurs in many parts of the United States, from coast to coast. They say such deficiency is especially important in the South Atlantic states (Virginia, North and South Carolina, Georgia, and Florida) and the Pacific states (Washington, Oregon, and California).

In recent years S responses have become more significant for legume pastures in Australia and New Zealand. Similarly, in Western Europe there has been increased S deficiency for such crops as rapeseed, cruciferous root crops, small grains, alfalfa, and other forage crops (Beaton and Fox, 1971).

In Canada, deficiencies of S have been largely confined to the western provinces of British Columbia, Alberta, Saskatchewan, and Manitoba (Beaton and Fox, 1971). Yield responses to S application on both legume and cereal crops have been obtained in Canada's four western provinces (Beaton and Fox, 1971; Beaton et al., 1966).

In Alberta, very large yield increases of legumes from S fertilization have been reported (Bentley et al., 1955; Chapman et al., 1972; Newton, 1936; Nyborg and Hennig, 1969; Sorensen, 1965; Wyatt, 1945). Alberta S deficiency has commonly occurred on Gray Luvisols. Prior to 1960, S response of legumes in Alberta was primarily on Luvisolic soils and Chernozemic areas associated with such soils. However, the responses were not confined to a specific soil series or definite geographic area (Walker and Bentley, 1961). Although most cereal grain

yield increases from applications of S bearing fertilizers have been confined to Gray Luvisols in the west central and north central part of Alberta (Beaton et al., 1966), there have also been striking results on such soils in the Peace River region (Bentley et al., 1971). Those reports have made it clear that S deficiency often occurs on soils that are also N deficient and that yield increases from S fertilization are frequently dependent on the simultaneous application of N (Bentley et al., 1971; Nyborg and Bentley, 1971). It has been found that N fertilization of rapeseed growing on S deficient soils may cause a decrease of seed yield compared to the nil treatment even though such N fertilization resulted in greater vegetative growth of the rape crop (Nyborg and Bentley, 1971).

Fertilizer and soil management recommendations for Alberta farmers emphasize the importance of appropriate S fertilization of soils deficient in that element because crop yields and quality are both likely to be improved very substantially by recommended practices (Bentley et al., 1971).

MATERIALS AND METHODS

1971 Field Experiments

These field experiments were placed in order to establish whether some Chernozemic soils in the Wainwright - Vermilion region, which had low values for available S by the ASFTL procedure, were S deficient under field conditions. A second purpose was to study the effect of S fertilization on plant composition.

The field experiments were placed in the Wainwright - Vermilion region in the summer of 1971. Some of the soil samples which had been submitted to ASFTL by the farmers from those areas for routine soil tests in the fall of 1970 were found to have low test values for available S. The criteria proposed for identifying S deficient soils have been described previously. In early May of 1971, soil samples were again taken from several farm fields which had previously been found to have low available S contents. The new samples were submitted to the ASFTL for available S determination. On the basis of those results, five sites, all of which had been cropped the preceeding year, were selected for plot experiments. For comparison purposes, field experiments were also placed on two Gray Luvisols known to be S deficient as tabulated in the Appendix (Table A).

The experiment plot plan was a randomized complete block design with three treatments and six replicates of each of three test crops. The fertilizer treatments were: nil, NPK, and NPKS where N, P, K, and S

were applied at rates of 110, 22, 44, and 22 kg per ha, respectively. Fertilizer applications per plot (2 m x 7 m, approximately) were as follows: N was applied as 413 g of 34-0-0 ammonium nitrate; P was applied as 344 g of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ containing 8.2 percent P; K was supplied as 113 g of 0-0-60 KCl; and S was supplied as 141 g of Na_2SO_4 which contains 22.5 percent S. Fertilizers were applied broadcast.

Ladak alfalfa, Galt barley, and Echo rapeseed were used as the test crops. Three test crops were used in the hope of ensuring that, if there were S deficiency at any of the sites, at least one crop would respond to S fertilization. Three crops would also give an opportunity to study response to S by different crops under similar conditions. There were eight rows of each crop in each replicate and seeding was done with a push-type Planet Junior planter. The space between rows was 23 cm. Yields were based on samples taken at maturity for barley and rapeseed. Alfalfa was harvested as hay about 100 days after seeding. The harvested sample was a rod row in each replicate (two rows at 23 cm spacings, and 2.5 m long were taken). Whole plant samples were weighed after air drying. Barley and rapeseed were threshed to separate the seeds. Foreign seeds were removed from barley grain and rapeseed at the time of threshing. Barley grain and rapeseed were weighed; then the values were subtracted from the weight of the whole plant to determine the weight of straw. Yields were expressed as quintals per hectare. Statistical calculations were made in accordance with Duncan's multiple-range test (Steel and Torrie, 1960).

For laboratory analyses representative straw samples of barley and rapeseed were taken at harvest time. The plant materials were oven

dried at 60°C for 48 hours; then ground using a Wiley laboratory mill. Plants were analyzed for total S, total N, P, Ca, and Mg. For analyses samples were ashed by wet digestion with perchloric-nitric acid (Johnson and Nishita, 1952). After solutions were made up to volume samples were taken for total S determination by Johnson and Nishita method (1952) as modified by Carson et al. (1972). Total P was determined by the vanadomolybdophosphoric yellow color method in nitric acid system (Jackson, 1958); Ca and Mg were determined with a Perkin Elmer 303 Atomic Absorption Spectrophotometer. Total N was determined by the macro-Kjeldahl method (Jackson, 1958), using a mixture of HgO, CuSO₄, and K₂SO₄ (Kel-pak) as catalyst.

There were some problems with the field experiments. Some plots, especially of alfalfa, were badly infested with weeds. It was not practical to hand weed all replicates of alfalfa and so yield data were based on only two or three replicates per treatment for that crop. At some locations germination of alfalfa seeds was also uneven. Only partial weeding of the rapeseed and barley was possible at some locations and, although all replicates were harvested, weediness had some adverse effects on final yields.

Greenhouse Experiment 1

This experiment was intended to ascertain whether soils from the study area respond to S fertilization under greenhouse conditions.

This study was done on soils from the Wainwright - Vermilion region also supplemented by two Gray Luvisols. Farmers from the Wainwright - Vermilion region had submitted soil samples to the ASFTL

some of which had shown low available sulfur. The Wainwright - Vermilion experimental soils were from such fields which were resampled in May, 1971, and retested by the ASFTL to ensure their relatively low available sulfur status. One of the Gray Luvisols was taken from Plot 4 of the Breton Plots where sulfur fertilizer had been applied at the rate of 15 kg of S per ha for over 30 years. The second Gray Luvisol was from a sulfur deficient field in the Peace River area.

In May, 1971, about 70 kg of each soil was taken from the surface 15 cm layer of the fields sampled. As soon as convenient, the soils were air dried and seived through a half centimeter screen. Soils were then stored in a cool place until the experiment was commenced in January, 1972. Samples from the prepared soils were submitted to the ASFTL for testing and on the basis of results obtained were classified into three catagories: soils of low available S (0-3 ppm); soils of medium available S (3-5 ppm); and soils of high available S (more than 5 ppm).

Galt barley was planted as the test crop with various fertilizer treatments being used. Fifteen centimeter plastic pots were filled to a comparable level with the various soils. The average soil weight was about 1,700 g per pot. All fertilizer treatments were made using chemicals of analytical grade to ensure purity. The treatments were as tabulated in Table 1. All fertilizers were applied in solution, 10 ml being applied for each nutrient or time. The initial N and S were mixed with the soil before it was placed in the pots. The P was placed as a band on the soil after the pots had been filled to a point 5 cm below the ultimate soil surface. Prior to applying the P, soils in the

Table 1. Nutrient Applications, Greenhouse Experiment 1

Nutrient	Chemical Used	Amount of Nutrient Element mg/pot	Time Applied
N	NH_4NO_3	204	At start of experiment
		204	40 days after seeding
		204	63 days after seeding
P, K	KH_2PO_4	85, 105	At start of experiment
S	Na_2SO_4	34	At start of experiment
		34	40 days after seeding
		34	63 days after seeding

pots were brought to field capacity and after P application each pot was brought to field capacity in accordance with data in the appendix, Table B. All watering was done with distilled water. Two seeds were put into each of seven equally spaced holes at a depth of 1.5 cm. To speed and encourage uniform germination the barley seeds were placed upright in the planting holes and covered with Ottawa sand which was kept moist during the germinating period.

The experiment was conducted in the greenhouse of the University of Alberta, chamber No. 12. Fluorescent light was used to supplement daylight giving 1,000 foot-candles during the seedling period and 600 foot-candles during the later growth stages. A 16-hour photoperiod was maintained. Temperature was controlled with a thermostat set at 20°C. Each pot was brought to apparent field capacity by weighing, daily. In

order to ensure uniformity of environmental conditions the pots were rotated frequently. Aphids were known to be a problem and so during the growth period a S-free insecticide, namely a chemical mixture of 0.02 percent pyrethrins, 0.13 percent rotenone, and 0.25 percent piperonyl butoxide in an aerosol form was applied periodically.

Growth differences between soils and between treatments of individual soils were evident within a few days and throughout the experiment. Thinning to seven seedlings per pot was done a week after planting. Two cuttings, each of two plants per pot, were made 35 days and 60 days after seeding. For those two samplings, oven dry weight of the combined three replicates of each treatment were determined and recorded. The fertilizer treatments caused some differences in maturity but on the average the final harvest was made 120 days after seeding. The heads and the straw were separated and weighed. The heads were threshed, employing a head thresher, followed by chaff separation to obtain the weight of full kernels.

Plant analyses were made for each of the three harvests. Nitrogen, P, S, Ca, and Mg were determined. Because of the very small quantities of material (Table 11) the first-cut plant samples were arranged into three groups on the basis of visible signs of response to S fertilization. Plant samples from corresponding treatments in each group were then combined in order to obtain sufficient sample amounts for analyses. Total N was determined by the semimicro-Kjeldahl method (Bremner, 1965). Phosphorus, S, Ca, and Mg were determined as described previously.

Towards the end of this experiment the aphid infestation was not satisfactorily controlled. The insects reappeared in increased

number shortly after each application of insecticide. As the crop was maturing the infestation was very much worse on those plants which were slowest to mature. For that reason the plants which received the NPK treatment were very severely affected and the other treatments were affected very little.

Greenhouse Experiment 2

This greenhouse experiment was undertaken in the hope of determining whether the low grain yields in the NPK treatment of greenhouse experiment 1 were caused by: too wide a N:S ratio; effects of delay in maturity caused by that fertilizer treatment; or the effect of an extreme aphid infestation which affected those late maturing plants.

The soils used were taken from the Wainwright - Vermilion region and from two plots of the University of Alberta experimental farm at Breton. Wainwright - Vermilion soils of low S status, as determined by ASFTL tests for available S were chosen. The soils from Breton were from Plot 4, which had received 15 kg of S per ha every second year for 40 years, and the adjacent Plot 5 which had had the same cropping pattern, but had never been fertilized. About 70 kg of each soil were taken from the sites in July, 1972, and they were processed as described in greenhouse experiment 1. For greenhouse experiment 2, the plastic pots were 19 cm ones and the amount of soil in each pot averaged about 2,500 g when pots were filled to comparable levels.

The experiment had five soils, each with five fertilizer treatments replicated three times. A randomized complete block design was employed. The fertilizer treatments were as shown in Table 2. The methods of fertilization described in greenhouse experiment 1 were employed again using chemicals of analytical grade quality.

Galt barley was again the crop grown. The method of seeding was the same as described for experiment 1, except that three seeds were placed in each of three holes. Thinning to three plants per pot was done a week after seeding.

This experiment was also conducted in the University of Alberta greenhouse, compartment No. 12. The seeding was done on August 2, 1972. Plants received only sunlight during the first two months. During the rest of the growing period supplemental fluorescent light was employed to maintain a 16-hour photoperiod as described for the first greenhouse experiment. Watering was also done as described previously (Appendix, Table I). Insecticides were again employed to control aphids. Pirimor 50 W insecticide was used once in addition to the same chemical mixture used in experiment 1. This aphid control program was quite effective. However, in this experiment mildew severely affected some of the plants during part of November and December. A fungicide was applied in an effort to control the mildew but success was only partial as reoccurrence was frequent.

Harvesting was done at maturity. Heads and straw were cut separately and weighed. Heads were threshed and the net filled grain weights were obtained as described for greenhouse experiment 1. The growth period for the crop ranged from 115 to 132 days being much affected by the fertilizer treatments: N_1PK and N_2PK treatments were

Table 2. Nutrient Applications, Greenhouse Experiment 2

Treatment ϕ	Nutrient Elements,* mg/pot				Time of Application
	N	P	K	S	
PK	--	125	155	--	At start
N ₁ PK	63	125	155	--	At start
	63	--	--	--	28 days
	63	--	--	--	51 days
N ₁ PKS	63	125	155	50	At start
	63	--	--	--	28 days
	63	--	--	--	51 days
N ₂ PK	250	125	155	--	At start
	250	--	--	--	28 days
	250	--	--	--	51 days
N ₂ PKS	250	125	155	50	At start
	250	--	--	--	28 days
	250	--	--	--	51 days

* Sources of nutrient elements:

N as NH_4NO_3 ; P and K as KH_2PO_4 ; and S as Na_2SO_4 .

ϕ N₁ is used to designate the lower rate of N application and N₂ to designate the higher rate.

so retarded in maturity that they were much more severely affected by mildew than the other treatments. The plants headed out 51 days after seeding. Chemical analyses were done on grain and straw samples by the methods described previously.

As stated, mildew instead of aphids was a serious problem in this experiment. The mildew infestation was quite heavy towards the end of the experiment, especially on the later maturing NPK treatments, partly because the fungicides which are most effective for its control could not be used because of their S content.

RESULTS AND DISCUSSION

Field Experiments

Yields of Rape, Barley and Alfalfa

Several available S tests were done on soil samples from sites of the 1971 field experiments. The data for samplings done by farmers in the fall of 1970, for re-sampling done May 1 - 5, 1971, and for samplings at seeding time and harvest are tabulated in Appendix Tables C, D, E, and F. Those data show the generally low values for available S in the soils concerned.

Yield results from the three test crops were used to determine if the fields concerned were S deficient for those crops. On the basis of results with the individual crops at each location there were a number of cases of S deficiency as can be seen from the data of Tables 3, 4, and 5. Results for grain and straw of two crops, rape and barley, show statistically significant yield responses to S in nine instances of a possible 28 and involving seven sites and two crops. The alfalfa yields are not very meaningful due to the small number of replicates sampled. Only location 7 in the Wainwright-Vermilion region appears to have shown response to S with all three test crops, but there was a similar trend at locations 3 and 5 which were on Luvisolic soils not in that region.

If, for each test crop the yield data of the seven locations are taken as replicates, the results of statistical analyses are

Table 3. Yield of Rape (in q/ha) for 1971 Field Experiments

Site No.	Straw			Seed		
	Nil	NPK*	NPKS*	Nil	NPK*	NPKS*
1	19.4a [†]	46.9b	48.1b	6.2a	16.8b	16.4b
2	13.5a	42.7b	44.3b	4.0a	14.3b	14.7b
3 ¹	16.5a	38.2b	57.1c	4.8a	3.5a	16.5b
4	24.8a	33.1b	37.1b	8.9a	11.7a	13.3a
5	16.5a	28.3a	57.0b	4.2a	7.6a	18.5b
6	6.9a	31.2b	38.1b	2.3a	9.9b	15.6c
7	16.6a	27.5b	38.6c	5.8a	3.3b	10.9c
Means, with sites as repli- cates	16.3a	35.4b	45.8c	5.2a	9.6b	15.1c

* The rates of N, P, K and S were added at 110, 22, 44, and 22 kg/ha, respectively.

† Values within rows not followed by the same letter differ at the 5% level for individual sites. (a, b, c).

¹ Only 2 replicates, as rain prevented complete seeding of experiment.

Table 4. Yield of Barley (in q/ha) for 1971 Field Experiments

Site No.	Straw			Grain		
	Nil	NPK*	NPKS*	Nil	NPK*	NPKS*
1	14.2a [†]	41.6b	40.9b	15.7a	42.8b	41.5b
2	10.5a	36.9b	40.7b	10.3a	35.4b	34.3b
3 ¹	30.8a	54.6a	69.1a	31.9a	46.6a	48.0a
4	17.6a	35.1b	34.2b	14.7a	35.6b	33.0b
5	7.6a	32.2b	38.6b	5.2a	34.4b	44.2b
6	8.5a	29.5b	28.2b	9.2a	26.4b	22.1b
7	11.4a	26.6b	34.7c	9.7a	21.6b	28.3c
Means with sites as replicates	14.4a	36.6b	40.9b	13.8a	34.7b	35.9b

* The rate of N, P, K and S were added at 110, 22, 44, and 22 kg/ha, respectively.

† Values within rows not followed by the same letter differ at the 5% level.

¹ Only 2 replicates, as rain prevented complete seeding of experiment.

Table 5. Yield of Alfalfa (in q/ha) for 1971
Field Experiments

Site No.	Treatments		
	Nil	NPK*	NPKS*
1 ¹	6.9a [†]	10.8a	14.5a
2 ³	8.1a	22.7b	22.3b
3 ¹	10.2a	16.6a	28.9a
4 ³	11.4a	16.4b	16.8b
5 ³	14.1a	11.4a	16.9a
6 ¹	10.5a	44.3b	49.3b
7 ²	5.3	9.0	12.3
Means with sites as replicates	9.5a	18.7b	23.0b

* The rate of N, P, K, and S were added at 110, 22, 44, and 22 kg/ha, respectively.

† Values within rows not followed by the same letter differ at the 5% level.

¹ Only 2 replicates sampled.

² Only 1 replicate sampled.

³ Only 3 or 4 replicates sampled.

somewhat different. Both rape straw and rape seed then show significant response to S fertilization (Table 3). Although the results with alfalfa do not reveal a statistically significant response to S, there is yield advantage of the NPKS treatment over the NPK treatment at every location. For barley straw there is a weak indication of S response on that basis but there is no such indication for barley grain. These data seem to support Nyborg's statement (1968) that cereals are less prone to show S deficiency than legumes. Similarly, cereals show less response to S deficiency than rape in this case when they are grown on the same soils. The results in Tables 3 to 5 suggest two conclusions. Firstly, of the three test crops rape may be the crop most likely to be affected by S deficiency if it is grown on fields with low tests for available S. Secondly, available S tests on farm soils have resulted in identification of S deficient fields in an area where that nutrient deficiency had not been expected or known to occur.

The substantial yield increases from the NPK and NPKS treatments of Tables 3 to 5 compared to the yields of the nil treatments are not surprising in view of the fact that all sites had been cropped in 1970. Figures 1, 2, and 3 show field results at site 7.

Laboratory Analyses of the Three Crops

The data for N, P, and S content of barley straw and grain, 1971 field experiments, are shown in Tables 6 and 7. It is apparent that S application had a larger effect on straw than on grain composition. The contents of S and P in the straw were affected by the



Figure 1. Barley (foreground) with NPKS, NPK and nil (L. to R.), and rape (background) with NPK, nil and NPKS (L. to R.) (Site 7)



Figure 2. Rape of Figure 1 at harvest time.



Figure 3. The difference of maturity of barley NPKS (left) and NPK (right). Barley of Figure 1, at harvest time.

Table 6. N, P, and S Content of Barley Straw, 1971 Field Experiments

Site No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
1	0.76	0.53	0.51	0.24	0.05	0.04	0.25	0.10	0.15
2	0.82	0.78	0.83	0.27	0.12	0.10	0.23	0.08	0.15
3	0.70	0.88	0.77	0.16	0.13	0.08	0.12	0.08	0.17
4	0.55	0.59	0.65	0.10	0.04	0.04	0.15	0.11	0.22
5	0.82	0.78	0.70	0.30	0.23	0.11	0.13	0.08	0.11
6	0.76	0.39	0.37	0.29	0.12	0.11	0.26	0.10	0.14
7	0.51	1.38	0.73	0.07	0.10	0.04	0.13	0.08	0.14

Table 7. N, P, and S Content of Barley Grain, 1971 Field Experiments

Site No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
1	1.83	2.20	2.13	0.39	0.34	0.33	0.13	0.13	0.14
2	1.76	2.10	2.34	0.39	0.36	0.37	0.14	0.12	0.14
3	1.73	2.09	2.17	0.36	0.40	0.37	0.10	0.07	0.11
4	2.11	2.45	2.55	0.39	0.31	0.32	0.13	0.15	0.15
5	2.05	2.08	1.87	0.42	0.39	0.37	0.12	0.10	0.10
6	1.66	1.73	1.76	0.38	0.37	0.37	0.11	0.11	0.11
7	1.70	2.72	2.34	0.33	0.36	0.33	0.10	0.10	0.13

fertilizers in consistently different ways. However, there was no consistent effect of treatments on the N content of straw although grain from the nil treatment tended to have the lowest content of N. The N and P contents of barley grain were considerably higher than in the straw but that was not true for S. This seems to suggest that if S was sufficient, adding N and P might increase yield; but under S deficiency, adding N might decrease grain yield as has been shown for wheat (Hausenbuiller, 1972). Holford (1971) has reported that during the early stages of growth, cereals can accumulate $\text{SO}_4\text{-S}$ in the vegetative tissues and that as seeds form some of that $\text{SO}_4\text{-S}$ is translocated to the heads. The low S content of barley straw from the NPK treatment of soils low in available S is probably due to translocation of S from the straw to form grain protein when there is an adequate supply of N for such protein formation. This is compatible with Holford's suggestion that the translocation of accumulated $\text{SO}_4\text{-S}$ to the developing inflorescences might account, at least partly, for the tolerance of cereals to low levels of S without reduction in grain yield under field conditions.

Tables 8 and 9 tabulate the content of N, P, and S in the straw and seed of the rape from the field experiments. In most cases, S content for both straw and seed was lower in the NPK treatment than in the other treatments. It appears that S application did not affect the content of N and P in straw or seed.

Analyses for the N, P, and S content for alfalfa at the pre-bloomed stage are reported in Table 10. Most of these S values are

Table 8. N, P, and S Content of Rape Straw, 1971 Field Experiments

Site No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
1	0.51	0.52	0.47	0.08	0.07	0.06	0.21	0.22	0.22
2	0.32	0.51	0.52	0.08	0.06	0.08	0.15	0.11	0.13
3	0.55	0.98	0.55	0.09	0.17	0.06	0.07	0.06	0.10
4	0.45	0.65	0.62	0.04	0.06	0.05	0.27	0.15	0.26
5	0.42	0.38	0.33	0.16	0.09	0.04	0.13	0.06	0.16
6	0.49	0.74	0.58	0.07	0.11	0.10	0.25	0.17	0.23
7	0.28	0.59	0.65	0.03	0.05	0.06	0.07	0.06	0.10

Table 9. N, P, and S Content of Rape Seed, 1971 Field Experiments

Site No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
1	3.18	3.85	3.84	0.78	0.81	0.79	0.63	0.64	0.64
2	3.06	3.56	3.75	0.82	0.81	0.79	0.58	0.57	0.65
3	3.04	3.54	3.48	0.73	0.95	0.78	0.29	0.16	0.55
4	3.66	4.12	4.23	0.73	0.78	0.78	0.73	0.67	0.80
5	2.82	3.20	3.08	0.92	0.89	0.83	0.51	0.28	0.56
6	3.40	3.44	3.37	0.78	0.80	0.79	0.63	0.57	0.60
7	3.12	3.86	4.17	0.71	0.81	0.78	0.54	0.37	0.69

Table 10. N, P, and S Content of Alfalfa, 1971 Field Experiments

Site No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
1	2.44	2.20	2.08	0.30	0.22	0.22	0.51	0.30	0.36
2	1.83	1.91	1.87	0.25	0.16	0.16	0.34	0.14	0.22
3	1.65	2.37	1.92	0.16	0.14	0.12	0.16	0.10	0.15
4	2.68	2.64	2.58	0.18	0.18	0.18	0.30	0.23	0.26
5	2.83	2.73	2.60	0.25	0.25	0.23	0.23	0.18	0.24
6	1.91	2.01	2.65	0.25	0.24	0.25	0.51	0.42	0.32
7	2.65	2.90	2.84	0.26	0.20	0.14	0.35	0.18	0.30

above the 0.2 percent S content suggested by Martin and Walker (1966) as a critical level below which S deficiency would occur. The N values found here are generally near or in the 2.72 - 2.98 percent N range which Cairns and Carson (1961) have suggested as the usual N content of alfalfa when it is grown on S sufficient soils.

The results of Ca and Mg determinations for the various crops and plant parts are in Appendix Tables J, K, and L. It was comparatively easy to do those determinations and they were done to ascertain whether the fertilizer treatments were having any consequential and/or consistent effects on plant compositions. No distinct differences or trends are evident in those tables. The data are included in the Appendix as a means of preserving them for possible future interest or need. The levels of Ca and Mg found in alfalfa were compared with levels reported by Chapman (1967). The Ca results reported here are in what Chapman has designated as the low range (below 1.5 percent) while the Mg data herein were generally in Chapman's medium range (0.20 to 0.25 percent) for that element.

Greenhouse Experiment 1

Yields of Barley Samples

Most soils used in the greenhouse experiment were taken from the Wainwright-Vermilion region but two Luvisolic soils were included for comparison purposes. Location and classification data are shown in

Appendix, Table A. The ASFTL soil analyses are given in Appendix, Table E.

Three harvests of barley for yields were taken. Table 11 shows the average yield of first cut barley taken 35 days after seeding. The crop in the low S test group of soils showed a consistent trend for yield increase of the NPKS treatment compared to the NPK treatment and there was a significant increase from S if those data are subjected to statistical analyses, with soils as replicates. By contrast, there were very small or no increases in the yield of the NPKS treatment compared to the NPK treatment for soils with medium or high test values for available S. Table 12 shows the average yield of barley cut 60 days after planting. The yield results for the three soil groups were the same as for the first cut; i.e., there was a significant yield increase (the average means) of the NPKS treatment over the NPK treatment in the low S group of soils, and there was no significant increases of yield in NPKS treatment compared to the NPK for soils with medium or high test levels of S. However, significant yield increases with the NPK treatment in all three groups, compared to the nil treatments, were again obtained. See Figures 4 and 5.

The yields of mature barley straw and grain are shown in Tables 13 and 14. The crop showed significant differences in yield of straw and grain on all soils in the low S level group when the NPK and NPKS treatments are compared. However, it is notable that in each case for the low S test soil group the NPK treatment caused inverse effects on straw and grain yields compared to the nil treatment; i.e., the straw yield was increased but the grain yield was decreased.

Table 11. Average Yield of First Cut Barley¹, Greenhouse Experiment 1

A. Soils which had available sulfur tests 0.0 - 3.0 ppm.

Soil No.	2	4	5	6	7	9	12	15	19	
Treatment	Yield, g/pot [†]									Mean
Nil	0.2	0.1	0.1	0.2	0.2	0.1	0.3	0.3	0.5	0.2A*
NPK	0.6	0.6	0.6	0.6	0.3	0.8	0.5	0.9	0.8	0.6B
NPKS	1.0	0.8	0.9	0.9	0.9	0.9	0.8	1.0	1.0	0.9C

B. Soils which had available sulfur tests 3.0 - 6.0 ppm.

Soil No.	3	8	20
Treatment	Yield, g/pot [†]		
Nil	0.3	0.2	0.6
NPK	0.7	0.2	0.7
NPKS	1.0	0.2	0.7

C. Soils which had available sulfur tests of more than 6.0 ppm.

Soil No.	10	13	16
Treatment	Yield, g/pot [†]		
Nil	0.2	0.7	0.6
NPK	0.3	1.0	0.9
NPKS	0.3	1.0	0.8

¹ Barley had been growing for 5 weeks.

[†] Average of 3 replicates from each of which 2 plants were taken.

* Values not followed by the same letters differ at 1% level. (A, B, C).

Table 12. Average Yield of Second Cut Barley¹, Greenhouse Experiment 1

A. Soils which had available sulfur tests 0.0 - 3.0 ppm.

Soil No.	2	4	5	6	7	9	12	15	19	
Treatment	Yield, g/pot [†]									Mean
Nil	0.7	0.2	0.5	0.5	0.3	0.4	0.6	0.8	1.1	0.6A*
NPK	1.9	1.9	1.2	1.2	1.0	1.9	1.1	1.7	1.5	1.5B
NPKS	4.5	3.4	4.1	4.2	4.0	4.3	4.6	5.4	4.4	4.3C

B. Soils which had available sulfur tests 3.0 - 6.0 ppm.

Soil No.	3	8	20	
Treatment	Yield, g/pot [†]			Mean
Nil	0.9	0.5	1.9	1.1a*
NPK	2.8	2.1	3.1	2.7b
NPKS	4.8	2.8	4.0	3.9b

C. Soils which had available sulfur tests of more than 6.0 ppm.

Soil No.	10	13	16	
Treatment	Yield, g/pot [†]			Mean
Nil	0.6	1.4	1.7	1.2A*
NPK	2.2	3.6	4.4	3.0B
NPKS	2.9	4.2	4.4	3.9B

¹ Barley had been growing for 8 weeks.

[†] Average of 3 replicates.

* Values not followed by the same letters differ at 1% level (A, B, C) or 5% level (a, b, c).



Figure 4. Effect of S on the growth of barley, soil 15, greenhouse experiment one.

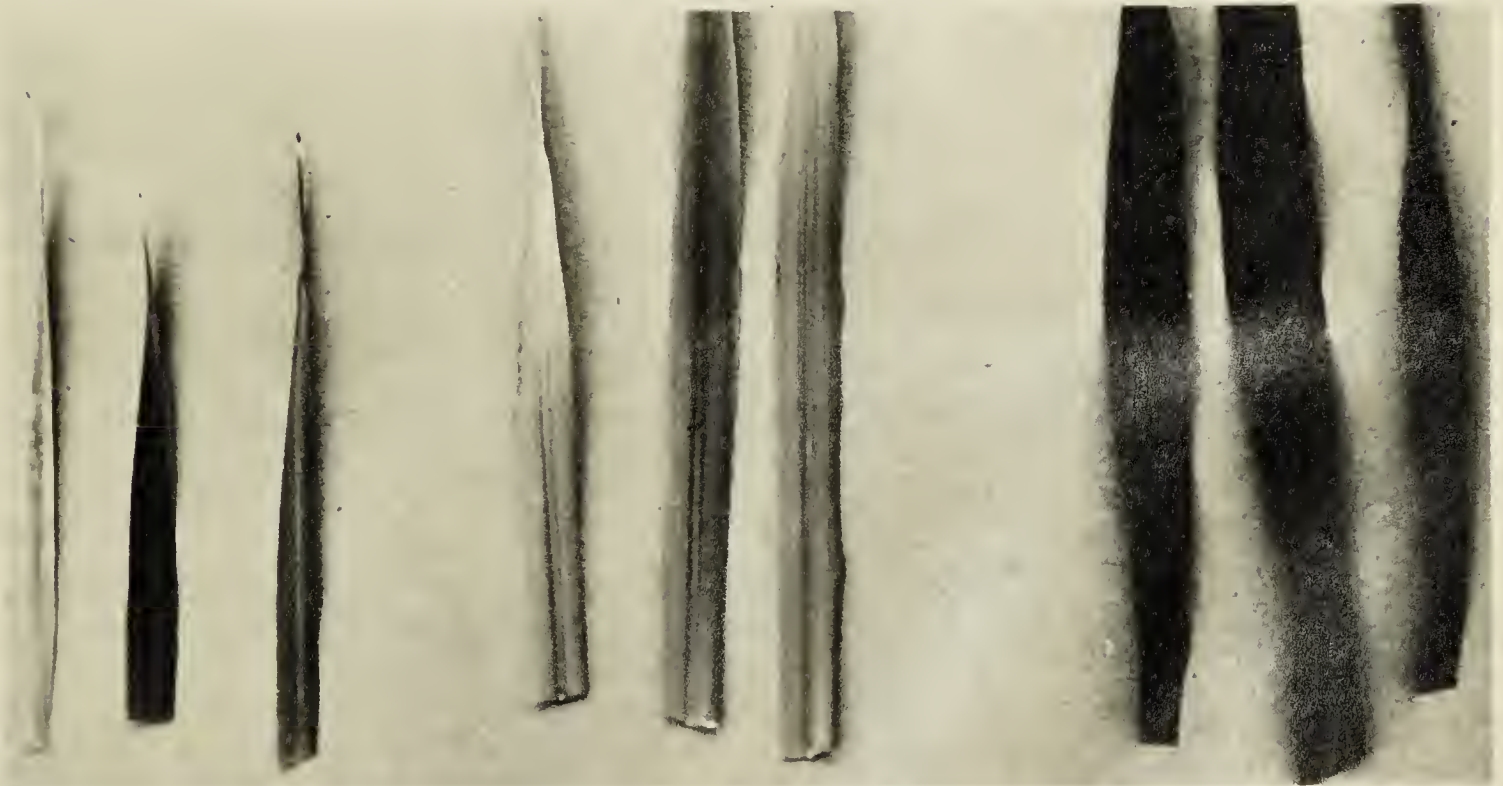


Figure 5. S deficiency. Color differences in barley leaves with Nil, NPK, and NPKS (L. to R.), Soil 4.

Table 13. Yield of Mature Barley Straw, Greenhouse Experiment 1

A. Soils which had available sulfur tests 0.0 - 3.0 ppm.

Soil No.	2	4	5	6	7	9	12	15	19
Treatment	Yield, g/pot †								
Nil	1.0a*	0.9a	1.3a	1.3a	0.9a	1.3a	1.5a	1.7a	2.1a
NPK	3.2b	4.4b	3.8b	3.8b	2.2b	4.3b	2.7b	5.5b	4.2b
NPKS	6.7c	9.2c	7.6c	7.7c	8.2c	8.3c	7.3c	8.9c	10.1c

B. Soils which had available sulfur tests 3.0 - 6.0 ppm.

Soil No.	3	8	20
Treatment	Yield, g/pot †		
Nil	1.7a	1.4a	3.1a
NPK	4.8b	6.4b	7.6b
NPKS	9.0c	9.7c	9.0b

C. Soils which had available sulfur tests of more than 6.0 ppm.

Soil No.	10	13	16
Treatment	Yield, g/pot †		
Nil	1.8a	3.5a	2.8a
NPK	7.2b	7.4b	7.9b
NPKS	7.4b	8.6c	8.4b

† Average of 3 replicates.

* Values within columns not followed by the same letter differ at the 5% level.

Table 14. Yield of Barley Grain, Greenhouse Experiment 1

A. Soils which had available sulfur tests 0.0 - 3.0 ppm.

Soil No.	2	4	5	6	7	9	12	15	19
Treatment	Yield, g/pot [†]								
Nil	1.1a*	1.0a	1.1a	1.2a	0.9a	1.3a	1.1a	1.8a	1.9a
NPK	0.4a	0.1b	0.2a	0.3b	0.1b	0.3b	0.1a	0.9a	0.6b
NPKS	8.0b	3.9c	7.5b	9.0c	1.0a	10.1c	10.1b	11.8b	1.6a

B. Soils which had available sulfur tests 3.0 - 6.0 ppm.

Soil No.	3	8	20
Treatment	Yield, g/pot [†]		
Nil	0.8a	1.4a	2.8a
NPK	1.0a	0.2a	1.6a
NPKS	11.8b	8.5b	8.2b

C. Soils which had available sulfur tests of more than 6.0 ppm.

Soil No.	10	13	16
Treatment	Yield, g/pot [†]		
Nil	0.6a	3.0a	2.8a
NPK	6.6b	3.5a	6.7b
NPKS	6.9b	9.3b	8.7b

[†] Average of 3 replicates.

* Values within columns not followed by the same letter differ at the 5% level.

For the medium S test group of soils, addition of S to the NPK treatment resulted in a significant increase in all cases for the grain yields but in only two of the three cases for the straw yields.

The NPK treatment increased only straw yield but not the grain compared to the nil treatment. Only one out of three soils, with a high S test value, showed significant S response in both straw and grain; the other two soils in that group did not show any significant increase of straw or grain yield from the NPKS treatment compared to the NPK treatment. However, the nil treatments were lowest in yield in all cases, as would be expected.

Some conclusions appear justified from the yield data of Tables 11 to 14 for greenhouse experiment 1. Under the condition of this experiment, responsiveness of the barley crop to S fertilization was related to the available S test values of the soils. On soils with low or medium levels of available S fertilization with NPK increased straw yields but with one exception decreased grain yields. Since the NPK treatment did not decrease grain yields on soils with high levels of available S it appears that NPK fertilization of soils deficient in S may adversely affect grain yields of barley in spite of increased straw yields resulting from such fertilization. Generally similar results have been reported for wheat by Hausenbuiller (1972), and for rapeseed by Nyborg and Bentley (1971). Moreover, similar data were obtained at site 7 of the 1971 field experiments (Table 3). The fact that some soils which did not show S response in the field did respond in the greenhouse is not surprising because the greenhouse yields

(equivalent of up to 68 q/ha of barley grain on an area basis) placed very heavy nutrient demands on the limited quantities of the soils used.

Laboratory Analyses

The first cut barley samples from greenhouse experiment 1 were combined into three groups based on visible S response and some analytical data are shown in Table 15. It should be noted that the contents of N, P, and S of the nil treatment increased with progression from soils of decreasing visible responsiveness to S. Comparing the effect of S added to the NPK treatment, there were inverse effects on the P and S content of plants from the three categories shown but there was no effect on N content.

Thus it appears that the visible response to S evident in plants at 35 days was accompanied by differences in the P and S level in the materials sampled at that time.

The second cut samples were analyzed for N, P, and S as reported in Table 16. On the low S level group of soils, the NPK treatment caused an increased N and decreased S level in plant material. The wider N:S ratios in this case are similar to those reported elsewhere (Allaway and Thompson, 1966; Cowling and Jones, 1971). The N:S ratios in Table 16 are inversely related to the available S content of the soils concerned.

Analyses from the second cutting show that N fertilization of soils with low available S widens the N:S ratio. That may have

Table 15. N, P, S, Ca and Mg Content of First Cut Barley Samples,
Greenhouse Experiment 1

% Element	Visible S Response								
	Good			Slight			None		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
N	2.45	4.66	4.82	3.42	4.89	5.14	3.63	5.39	5.61
P	0.12	0.76	0.40	0.37	0.56	0.47	0.41	0.30	0.50
S	0.29	0.13	0.39	0.38	0.19	0.42	0.51	0.37	0.42
Ca	0.84	1.12	0.77	0.87	0.95	0.77	0.77	0.77	0.70
Mg	0.33	0.26	0.26	0.32	0.31	0.27	0.30	0.32	0.27

Table 16. N, P, and S Content of Plant Material from the Second Cutting,
Greenhouse Experiment 1

Soil No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
<u>Low S Test</u>									
2	1.28	4.45	2.30	0.36	0.46	0.29	0.26	0.08	0.34
4	1.35	3.77	2.71	0.28	0.55	0.40	0.33	0.06	0.33
6	1.37	5.29	2.40	0.30	0.53	0.32	0.18	0.06	0.29
9	1.42	3.93	2.26	0.33	0.37	0.24	0.36	0.06	0.34
12	1.29	5.12	2.58	0.25	0.53	0.28	0.18	0.06	0.28
<u>Medium High S Test</u>									
10	1.77	4.17	4.18	0.26	0.35	0.30	0.44	0.34	0.41
13	1.26	2.68	2.69	0.30	0.38	0.32	0.18	0.12	0.38
16	1.09	2.27	2.45	0.38	0.37	0.27	0.34	0.18	0.37
20	1.17	2.66	2.74	0.27	0.44	0.33	0.18	0.08	0.31

adverse effects on N utilization for elaboration of protein in such plants (Coleman, 1966; Jordan, 1964; Renner et al., 1953).

The effect of S added to the NPK treatment on the content of N, P, and S of mature barley straw (Table 17) was similar to its effect on the second cut samples. In this case P content in the NPKS treatment was substantially depressed. However, the anion balance within that material was approximately maintained because S content was high when P was low, and vice versa.

Because of no or very little grain formation with the NPK treatment, analyses of grain from that treatment were not possible except in the case of some of the soils with high test values for available S (Table 18).

Thus, in this greenhouse experiment, S application did increase the grain yield but did not appreciably alter grain composition although the straw composition was altered, as was the case previously for that material. These results seem to support Beaton's (1966) and Bentley et al. (1955) statement that barley grain protein was less altered by lack of S than the S content of straw.

Calcium and Mg content for the second cutting, as well as for mature straw and grain of barley are shown in Appendix, Tables M and N.

The recoveries of applied S and N in greenhouse experiment 1 are shown in Tables 19 and 20. It should be noted that at the commencement of the experiment the group of soils with higher values for available S also had higher N than the group of low S soils. Plants growing in soils with medium to high levels of available S took up more N and S than those growing in the soils with low test values for S,

Table 17. N, P, and S Content of Barley Straw, Greenhouse Experiment 1

Soil No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
<u>Low S Test</u>									
2	0.54	4.74	0.61	0.30	0.34	0.03	0.30	0.05	0.55
4	0.42	4.12	0.74	0.33	0.34	0.12	0.29	0.04	0.28
6	0.56	4.58	0.65	0.11	0.28	0.04	0.06	0.05	0.24
9	0.51	4.10	0.63	0.17	0.32	0.03	0.30	0.06	0.40
12	0.31	5.41	0.75	0.16	0.32	0.03	0.10	0.04	0.33
<u>Medium-High S Test</u>									
10	0.54	1.10	1.00	0.04	0.02	0.03	0.54	0.16	0.45
13	0.38	1.76	1.04	0.17	0.19	0.04	0.15	0.08	0.58
16	0.53	0.98	0.90	0.32	0.05	0.03	0.46	0.06	0.58
20	0.43	2.80	0.64	0.28	0.39	0.05	0.14	0.05	0.40

Table 18. N, P, and S Content of Barley Grain, Greenhouse Experiment 1

Soil No.	% N			% P			% S		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
<u>Low S Test</u>									
2	1.56	--	1.66	0.49	--	0.37	0.12	--	0.20
4	1.61	--	3.12	0.48	--	0.57	0.12	--	0.20
6	1.58	--	2.60	0.44	--	0.40	0.12	--	0.17
9	1.50	--	2.37	0.45	--	0.37	0.12	--	0.18
12	1.73	--	2.55	0.33	--	0.20	0.12	--	0.17
<u>Medium-High S Test</u>									
10	2.11	3.19	2.91	0.49	0.33	0.32	0.16	0.17	0.20
13	1.39	2.99	2.68	0.28	0.41	0.28	0.12	0.08	0.17
16	1.58	2.64	2.67	0.34	--	0.45	0.12	0.12	0.20
20	1.42	3.27	2.72	0.42	0.56	0.39	0.12	0.10	0.18

Table 19. Result of S Accounting Calculations, Selected Soils
Greenhouse Experiment 1

Soil No.	Avail. SO ₄ -S in Soil mg/pot	Avail. SO ₄ -S at Start*	S Removals in Plant Materials† mg/pot			Avail. SO ₄ -S in Soil at End of Expt.‡		
			Nil	NPK	NPKS	Nil	NPK	NPKS
<u>Low S</u>								
2	6	108	6	3	68	3	2	6
4	6	108	4	3	45	4	3	31
6	5	107	3	3	46	4	0	27
9	7	109	7	4	66	3	3	8
12	5	107	4	2	54	3	2	7
<u>Medium-High S</u>								
10	40	142	13	30	59	24	6	40
13	11	113	11	13	82	5	3	9
16	17	119	22	21	82	5	3	15
20	10	112	11	6	63	3	3	8

* This is the sum of available SO₄-S in the soil plus the 102 mg added as fertilizer, where applicable.

† This includes removals in the second and final harvests.

‡ This is available S by the same procedure as at start.

Table 20. Results of Nitrogen Accounting Calculations, Selected Soils
Greenhouse Experiment 1

Soil No.	Total NH_4^+ and NO_3^- in Soils mg N/pot	Total Avail. N at Start* mg/pot	N Removals in Plant Materials† mg N/pot			Total NH_4^+ and NO_3^- in Soils at end of Expt.‡ mg N/pot		
	Nil		NPK	NPKS	Nil	NPK	NPKS	
Low S Test								
2	15	627	32	236	277	6	196	18
4	8	620	23	253	283	5	84	28
6	9	621	33	238	385	2	192	18
9	12	624	32	251	389	8	98	10
12	8	620	31	202	431	4	213	12
Medium-High S Test								
10	54	666	33	381	396	14	42	36
13	107	719	73	331	391	20	56	30
16	87	699	78	354	416	21	28	24
20	94	706	75	348	390	12	64	20

* This is the sum of NH_4^+ and NO_3^- in the soil plus the 612 mg added as fertilizer, where applicable.

† This includes removals in the second and final harvests.

‡ The sum of NH_4^+ and NO_3^- .

as would be expected. In some cases S removals in grain and straw exceed the available S in the soil at commencement of the experiment. In addition, some S would have been incorporated into the plant roots which were not removed. Such differences were due to mineralization of organic matter during the course of the experiment. With low available S in soils, application of NPK resulted in a substantial amount of available N remaining in soils at the end of the experiment. Thus, addition of S to the group of low S soils increased the utilization of applied N.

Conclusions drawn from this greenhouse experiment include:

1. Nearly all soils showed S deficiency under the controlled conditions of this experiment.
2. The extent of plant response to S fertilization is related to the available S levels found by the ASFTL tests.
3. Application of N without S to soils low in available S resulted in increased vegetative growth but decreased grain production.
4. Plant contents of N, P, and S were affected by fertilizer treatments, especially by S application.

Additional analyses performed on soils from the field and the greenhouse experiments are shown in Table 21. Drying of soil samples prior to making available S determination affected the content of available $\text{SO}_4\text{-S}$ found. When the same extractant was used, moist samples gave lower S content values than did dry samples in all cases. Similar results were reported elsewhere (Freney, 1958; Walker, 1972). The two sets of values in this case, however, were very highly correlated ($r = 0.98$). Walker (1972) recommended using air dry soil samples

Table 21. Some Analytical Data for Soils of Field Experiments and Greenhouse Experiment 1

Soil No.		Available S, ppm			% N
		With CaCl_2 Extractant		With KH_2PO_4 Extractant	
		Moist*	Air Dry	Air Dry	
Greenhouse	Field				
2	2	2.3	3.3	3.9	0.26
3	4	2.9	3.9	4.1	0.30
4	6	2.9	3.2	3.0	0.11
5	-	2.0	3.0	-	0.23
6	7	1.5	2.4	2.0	0.13
7	-	0.5	1.9	-	0.08
8	1	3.8	5.7	6.0	0.34
9	-	2.6	4.7	-	0.22
10	-	26.0	26.0	30.4	0.14
12	5	2.6	3.1	2.5	0.08
13	-	6.6	7.0	4.0	0.37
15	-	0.5	5.4	-	0.17
16	-	8.0	10.6	10.0	0.28
19	-	1.5	2.4	-	0.11
20	-	3.2	6.5	-	0.31

* Analyzed by ASFTL.

for S tests intended to be the basis for fertilization recommendations; such a procedure minimizes variability resulting from mineralization occurring in moist soils because of differences in time between sampling date and analytical determinations. There was very little difference between the S content of air dry soils extracted by CaCl_2 solution (ASFTL extractant) and the ones extracted by the KH_2PO_4 solution. Walker (1972) has reported similar results. The available SO_4 -S values in either moist soils or dry soils were not closely correlated with the N content of the samples tested. Excluding soil No. 10 (because of its high content of available S from long term fertilization) the correlation coefficient between total N and available S as determined on moist soil samples was 0.64; the correlation coefficient between total N and available S determined on dry soil samples was 0.66. Thus, total N was not a very satisfactory indicator of available S in these soils.

Greenhouse Experiment 2

Yield of Barley

The objectives of the second greenhouse experiment were somewhat different to those of the first one as already mentioned. Soil samples used are described in Appendix, Table G. Those objectives were not achieved as is shown by the yield data for the grain and straw shown in Table 22. Although straw yield with N_2 fertilization was significantly lower than straw yield with that fertilization plus S on

Table 22. Average Yield of Barley, Greenhouse Experiment 2, gram per pot.

Soil No.	Straw ϕ					Grain ϕ			
	PK	N ₁ PK	N ₁ PKS	N ₂ PK	N ₂ PKS	PK	N ₁ PK	N ₁ PKS	N ₂ PK
A - 1	1.1D**	4.3C	4.5C	8.6B	11.2A	1.4c*	6.4b	6.6b	7.8b
A - 2	1.1D	3.8C	4.1C	8.0B	10.0A	1.5c	6.2b	6.9b	6.2b
A - 3	3.5D	6.8C	7.3C	12.0B	14.9A	4.7d	9.2b	9.3b	6.9c
A - 4	1.4D	4.2C	5.0C	9.3B	12.1A	1.5c	6.7b	7.7b	9.9a
A - 5	5.4D	10.9C	11.2C	15.9B	19.2A	5.2c	12.3b	12.7b	16.7a

ϕ Average of 3 replicates.

* a - d. Values within rows not followed by the same letter differ at the 5% level.

** A - D. Values within rows not followed by the same letter differ at the 1% level.

all five soils, there were three cases where grain yield was significantly lower with N_2 fertilization than with N_2S fertilization. Moreover, there were no significant yield differences between N_1 and N_1S fertilization for either straw or grain on any of the five soils.

During the early stages of this greenhouse experiment, the plants showed symptoms of S deficiency at both rates of N application. However, plants, even at the higher rate of N, appeared to have recovered and to be normal at the pre-heading stage. It is doubted that the plants obtained S from other sources, such as water or SO_2 gas in the air, although that is a possibility. Therefore, these results and observations are different to those of greenhouse experiment 1 and remain unexplained. The data from this second greenhouse experiment do show that an adequate supply of available N is necessary for soils of low S status to respond to S fertilization. Beaton et al. (1966) as well as Nyborg and Bentley (1971) have reported such results in field experiments.

Laboratory Analyses of Plant Materials

The N and S contents of barley straw and grain from the second greenhouse experiment are shown in Tables 23 and 24. Those data show that the composition of straw was altered more by the fertilizer treatments than grain, as was found in the other experiments reported herein. The S content of grain was slightly changed by S fertilization in combination with the high rate of N fertilization. The N content of barley straw was approximately twice as high in the N_2PK treatment as

Table 23. N Content of Barley, in percent, Greenhouse Experiment 2

Soil No.	Straw ^φ					Grain ^φ				
	PK	N ₁ PK	N ₁ PKS	N ₂ PK	N ₂ PKS	PK	N ₁ PK	N ₁ PKS	N ₂ PK	N ₂ PKS
1	0.59	0.59	0.62	3.07	1.64	1.96	2.28	2.29	3.15	3.37
2	0.60	0.59	0.53	3.55	1.77	1.72	1.92	2.05	3.12	3.51
3	0.78	0.58	0.52	3.02	1.35	1.72	2.02	2.06	3.13	3.57
4	0.98	0.56	0.46	2.50	1.42	2.18	2.39	2.13	2.52	2.84
5	0.71	0.40	0.38	1.12	0.86	1.84	1.82	1.79	3.07	2.97

φ Analyses on combined samples of three replicates in each case.

Table 24. S Content of Barley, in percent, Greenhouse Experiment 2

Soil No.	Straw ^φ					Grain ^φ				
	PK	N ₁ PK	N ₁ PKS	N ₂ PK	N ₂ PKS	PK	N ₁ PK	N ₁ PKS	N ₂ PK	N ₂ PKS
1	0.26	0.12	0.30	0.06	0.28	0.10	0.12	0.12	0.11	0.16
2	0.28	0.09	0.26	0.06	0.25	0.12	0.12	0.12	0.12	0.18
3	0.41	0.13	0.29	0.06	0.19	0.12	0.11	0.12	0.12	0.15
4	0.46	0.15	0.34	0.05	0.22	0.12	0.12	0.14	0.08	0.14
5	0.33	0.12	0.19	0.06	0.18	0.11	0.10	0.12	0.10	0.15

φ Analyses on combined samples of three replicates in each case.

in the NPKS treatment. Nitrogen content of the grain was higher with the N_2 PKS treatment than was the case with the N_2 PK fertilization. These results suggest that protein formation in the grain is limited by the available S when nitrogen is not in limited supply. The N:S ratios in straw have a range of 19:1 to 59:1 with the N_2 PK treatment compared to a range of 5:1 to 7:1 with the N_2 PKS fertilization. The corresponding ranges in the grain were from 26:1 to 32:1 for the N_2 PK and 20:1 to 24:1 for the N_2 PKS treatment.

Those data show conclusively that fertilization of S deficient soil has a much greater effect on the composition of barley straw than on the composition of the grain. Straw of wide N:S ratio is likely to be of inferior nutritive value if fed to ruminants (Allaway and Thompson, 1966).

SUMMARY AND CONCLUSIONS

The results of these investigations can be conveniently summarized in five sections.

Field Experiments

There were statistically significant yield increases at two of the five Chernozemic soil locations and at both of the Luvisolic soil locations. Because of weed competition, alfalfa yields were not very meaningful as only one or two replicates were harvested at most locations. Rape responded to S fertilization at four of the seven locations whereas S fertilization of barley resulted in only one case of significant yield increase. Fertilization with NPK resulted in a slight but not significant decrease of rape seed yield compared to nil at two of the four locations where S fertilization increased yield of that crop, although the NPK fertilization increased vegetative growth of rape at those sites.

Greenhouse Experiment 1

Under the conditions of the first greenhouse experiment, twelve of the fifteen soils responded to S fertilization but the amount of yield increase tended to vary with the available S status of the soils. Although delayed crop maturity and aphid infestation were complicating factors, in soils fertilized with NPK barley grain yields were significantly decreased by that treatment on five soils in spite

of significant increases in vegetative growth from that fertilization on all fifteen soils.

Greenhouse Experiment 2

Although unexplained complications affected this experiment it supports results of other experiments which have found that an adequate amount of available N is a prerequisite to S response on soils of low available S content.

Plant Analyses

Fertilization treatments affected the composition of plant materials in the field and greenhouse experiments. Of the nutrients determined N and S contents were most affected by the fertilizer treatments but not to the same extent in the various crops or plant parts. Fertilization had the least effect on alfalfa composition and the greatest effect on barley composition. Sulfur content of barley straw from soils low in available S was substantially increased by S fertilization but the S content of barley grain from the same plants was little affected.

Conclusions

There are several conclusions from these investigations.

1. The available S test in use by the ASFTL has resulted in identifying some S responsive Chernozemic soils in the Wainwright-Vermilion region where S deficiency had not been anticipated. However, not

all soils of low S status responded to S fertilization under the conditions of the field experiments.

2. In the greenhouse soils of low S status all responded to fertilization with S and that confirmed the usefulness of the test in identifying soils low in available S.
3. Fertilization with NPK of rape and barley growing on S deficient soils in field and greenhouse experiments, respectively, has resulted in some yield decreases of rape seed and barley grain compared to no fertilization. Therefore, farmers applying N without S fertilization on S deficient soils may suffer yield decreases from such fertilization in spite of conspicuous yield increases of the vegetative growth of the crops concerned.
4. Nitrogen fertilization of barley on soils deficient in S results in substantial decreases in the S content of barley straw. Because of the wide N:S ratio in such straw it may be of low nutritive value if fed to ruminants.
5. Adequate supplies of available N appear to be requisite for plant response to S fertilization of soils low in available S content.

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APPENDIX TABLES

Table A. Identity, Location, and Classification of Soils for 1971 Field Experiments and of Soils Used for Greenhouse Experiment 1

Greenhouse Soil						
No.	Farmer's Name	Legal Location	Soil Order	Subgroup	Parent Material	Texture
2	Eyben, H. A.	NW 16-47- 7-W4	Chernozemic	Orth. Bl.	Glacial till	Clay loam
3	McTurk, F. R.	SW 1-45- 5-W4	Chernozemic	Orth. Dk. Br.	Glacial till	Loam
4	Sutter, J.	SW 7-44-12-W4	Chernozemic	Orth. Dk. Br.	Alluvial	Loamy sand
5	Hicox, C. A.	NE 22-46- 5-W4	Chernozemic	Orth. Dk. Br.	Alluvial	Sandy loam
6	Taylor, B.	NW 8-43- 8-W4	Chernozemic	Rego. Dk. Br.	Alluvial	Loamy sand
7	Harder, G.	NW 36-46- 9-W4	Chernozemic	Eluviated Dr. Br.	Alluvial	Loamy sand
8	Chesterman, A.	NW 3-48- 7-W4	Chernozemic	Orth. Bl.	Alluvial on till	Sandy clay loam
9	Paradis, D.	NE 36-44- 5-W4	Chernozemic	Orth. Dk. Br.	Lacustrine	Loam
10	Breton, A4-B4	NE 25-47- 3-W5	Luvisolic	Orth. Gr. Wd.	Glacial till	Loam
12	Nymoen, A.	NE 25-78-18-W6	Luvisolic	Bisequa Gr. Wd.	Alluvial on till	Silt loam
13	Stewart, G.	SW 31-50- 7-W4	Chernozemic	Orth. Bl.	Glacial till	Loam
15	Craigmillar Farm Ltd.	NW 22-38- 7-W4	Chernozemic	Orth. Dk. Br.	Alluvial	Sandy loam
16	Sieger, W.	NE 22-37-10-W4	Chernozemic	Orth. Dk. Br.	Glacial till	Loam
19	Charlton, N.	SW 18-39- 6-W4	Chernozemic	Rego. Dk. Br.	Alluvial	Sand
20	Hart, B.	SE 22-50- 7-W4	Chernozemic	Orth. Bl.	Glacial till	Sandy loam

Table B. Moisture and Weight Data for Soils of Greenhouse Experiment 1

Soil No.	Farmer's Name	Soil Weight g/pot	Hygroscopic Moisture, %	Water Content at F.C., %
2	Eyben	1,760	2.9	23
3	McTurk	1,470	3.8	30
4	Sutter	1,870	1.1	17
5	Hicox	1,720	1.9	25
6	Taylor	2,000	0.9	15
7	Hearder	2,120	0.5	12
8	Chesterman	1,580	3.0	27
9	Paradis	1,580	3.1	25
10	Breton # 4	1,530	2.2	24
12	Nymoen	1,600	1.2	19
13	Stewart	1,520	3.6	28
15	Craigmillar	1,720	2.2	20
16	Seiger	1,620	3.0	25
19	Charlton	1,780	0.7	22
20	Hart	1,520	2.3	25

Table C. ASFTL Analyses on Soils Submitted by Farmers in the Wainwright - Vermilion Region
During the Fall of 1970

Site No.	Locations and Farmer's Name	Previous Crop	Soil Test						O.M.	Texture*
			Lb/Ac			ppm SO ₄ -S	pH			
			N	P	K					
1	Eyben, H. A.									
	NE 17-47- 7-W4	Fallow	67	29	562	6.0	5.8	M-	3-	
	NW 16-47- 7-W4	Barley	5	36	496	2.4	6.2	M-	2-	
2	McTurk, F. R.									
	SE 1-45- 5-W4	Fallow	31	18	604	3.6	7.3	L+	2-	
	NE 1-45- 5-W4	Fallow	35	15	602	3.6	7.1	L+	3-	
3	Sutter, J.									
	NE 31-43-10-W4	Fallow	15	26	430	9.4	6.2	M-	2-	
	SE 31-43-10-W4	Fallow	7	25	350	1.2	6.1	M-	2-	
	SE 7-44-12-W4	Fallow	5	30	355	2.4	6.0	M-	2-	
	SE 7-44-12-W4	Fallow	7	32	370	2.4	6.0	M-	2-	
4	Taylor, B.									
	NW 8-43- 8-W4	Rye	5	23	224	2.4	6.3	M-	1	
	NE 8-43- 8-W4	Fallow	28	29	238	3.6	6.1	L+	1	
	NW 10-43- 8-W4	Fallow	7	17	300	2.4	7.4	M-	1	
	NW 3-43- 8-W4	Fallow	3	33	225	1.2	6.4	L+	1	
	NW 3-43- 8-W4	Alfalfa and brome	0	32	235	2.4	6.2	L+	1-	

* Texture is described as follows: 1 - very coarse; 2 - coarse; 3 - medium.

Table D. ASFTL Analyses on Soils from Fields Sampled May 1 - 5, 1971

Site No.	Location and Farmer's Name	Crop, 1970	Avail. $\text{SO}_4\text{-S}$ ppm
1	NW 3-48- 7-W4 Chesterman, A.	Wheat	0.0
2	NW 16-47- 7-W4 Eyben, H. A.	Barley	0.0
3	SW 29-47- 3-W5 Hanson, H.	Greenfeed	0.0
4	SW 1-45- 5-W4 McTurk, F. R.	Wheat	0.0
5	NE 25-78-18-W6 Nymoen, A.	Barley	--
6	SW 7-44-12-W4 Sutter, J.	Rape	0.0
7	NW 8-43- 8-W4 Taylor, B.	Rye	0.0
8	SE 13-45- 5-W4 McTurk, J. W.	Rape	5.0
9	SW 13-45- 5-W4 McTurk, J. W.	Wheat	0.0
10	NE 36-44- 5-W4 Paradis, D.	Wheat	0.0
11	NW 36-46- 9-W4 Hearder, G.	Rape	0.0
12	NE 22-46- 5-W4 Hicox, C. A.	Wheat	0.0

Table E. Initial ASFTL Soil Test Data, Field Experiments at Seeding and Greenhouse Experiment 1

A. Low Sulfur Group[†]

Determination	Soils								
	2 (2)*	4 (6)	5	6 (7)	7	9	12 (5)	15	19
N lb./ac.	7	5	6	6	3	5	6	18	36
P lb./ac.	25	57	20	19	40	17	36	22	50
K lb./ac.	403	470	361	253	127	612	334	551	446
S ppm	2.3	2.9	2.0	1.5	0.5	2.6	2.6	0.5	1.5
pH	6.6	5.9	6.2	6.4	6.1	6.6	6.4	6.4	5.7
Organic Matter	M-	L+	L+	L	L-	L+	L	L+	L+
Texture	3	1	2	1	1	5	5	3	1

B. Medium and High Sulfur Groups[†]

Determination	Soils					
	Medium Sulfur Group			High Sulfur Group		
	3 (4)	8 (1)	20	10	13	16
N lb./ac.	15	5	80+	19	75	64
P lb./ac.	37	28	62	27	96	145
K lb./ac.	620	415	460	231	521	1,219
S ppm	3.2	3.8	3.2	26.6	6.6	8.0
pH	7.2	5.8	5.7	5.6	5.7	5.2
Organic Matter	L+	M-	M-	L	M-	L+
Texture	3	4	2	3	3	3

[†] Soils with sulfur tests of less than 3 ppm were classified as low; 3 to 5 as medium; and above 5 as high.

* () Field experiments were placed.

NOTES: All conductivity values in the low sulfur group were 0.2 mmhos except one (4) was 0.1 mmhos; for medium and high sulfur group conductivity ranged from 0.2 - 0.5 mmhos. All samples tested L or L- for Na.

Table F. ASFTL Soil Test Data for Air Dry Soil Samples Taken at Harvest From Nil Treatments of 1971
Field Experiments

Farmer's Name		Chesterman									Eyben								
Plant at Site		Alfalfa			Barley			Rape			Alfalfa			Barley			Rape		
Depth*		A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
<u>Determination</u>																			
P, lb/ac	23	6	7	19	7	6	27	6	6	26	4	4	31	6	3	23	4	2	
K, lb/ac	380	239	239	374	253	308	448	262	260	376	246	260	381	216	207	357	279	275	
S, ppm	3.5	2.3	1.5	2.0	2.3	2.0	3.5	2.0	1.0	2.0	2.0	1.5	2.3	1.0	1.0	1.5	1.0	1.0	
pH	6.2	6.6	7.0	6.3	6.6	7.2	6.2	6.5	7.4	6.4	6.4	7.5	6.3	6.6	7.4	6.5	6.7	7.7	
Organic Matter	M	M-	L+	M	L+	L	M-	L+	L	M-	L+	L	M-	L+	L	M-	L+	L	
Texture	3	3	5	3	5	5	3	5	5	3	5	5	3	5	5	3	5	5	

*A = 0 - 6"; B = 6 - 12"; C = 12 - 24" depths

NOTES: Most N values were 0 or 1; four values were 2; all samples tested L or L- for Na; all conductivity values for surface samples were 0.1 or 0.2 mmhos and the highest values for subsurface samples were 0.5 mmhos. No samples were calcareous in the Ap layer.

Texture is described as follows:
1. very coarse; 2. coarse;
3. medium; 4. fine;
5. very fine.

Table F. (Continued)

Farmer's Name	McTurk						Nymoan											
	Alfalfa			Barley			Rape			Alfalfa			Barley			Rape		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
<u>Determination</u>																		
P, lb/ac	8	2	0	17	2	0	11	4	2	44	13	1	38	14	0	40	20	5
K, lb/ac	635	526	448	261	470	415	548	435	465	212	282	160	175	175	256	166	191	225
S, ppm	2.9	3.5	2.6	2.6	2.3	1.5	2.3	1.5	2.0	1.0	0.5	1.5	1.5	1.5	1.0	0.5	1.0	1.5
pH	7.0	8.0	8.5	6.6	7.7	8.2	7.4	7.5	8.1	6.9	7.0	7.5	6.8	7.0	7.6	6.9	6.7	7.3
Organic Matter	L+	L+	L	L+	L+	L	M-	L+	L	L	L	L	L	L	L	L	L	L
Texture	3	5	5	3	5	5	5	5	5	4	5	5	4	5	5	4	5	5

Table F. (Continued)

Farmer's Name	Sutter						Taylor					
	Alfalfa		Barley		Rape		Alfalfa		Barley		Rape	
Plant at Site	Alfalfa	Barley	Alfalfa	Barley	Rape	Rape	Alfalfa	Barley	Alfalfa	Barley	Rape	Rape
Depth*	A	B	C	A	B	C	A	B	C	A	B	C
<u>Determination</u>												
P, lb/ac	47	18	7	46	15	9	47	16	6	25	11	15
K, lb/ac	394	369	343	454	388	480	470	372	388	245	130	142
S, ppm	2.3	1.0	1.5	1.0	1.5	1.5	1.0	2.0	1.5	1.0	1.0	1.0
pH	6.3	6.3	6.9	6.3	6.5	7.1	5.9	6.2	6.9	6.2	6.4	6.5
Organic Matter	M-	M-	L	M-	L+	L	M-	M-	L	L+	L+	L-
Texture	1	1	3	1	1	5	1	1	3	1	1	1

Table G. Identification and Classification of Soils, Greenhouse
Experiment 2

Soil No.	Legal Location	Soil Order	Subgroup	Parent Material
A-1	NE 25-47-3-W5	Luvisolic	Orthic Gr. Wd.	Glacial till
A-2	NE 25-47-3-W5	Luvisolic	Orthic Gr. Wd.	Glacial till
A-3	NH 22-46-5-W4	Chernozemic	Orthic Dk. Br.	Alluvial
A-4	NE 16-52-7-W4	Chernozemic	Orthic Black	Lacustrine
A-5	NW 5-46-6-W4	Chernozemic	Orthic Black	Alluvial

Table H. ASFTL Soil Test Data for Air Dry Soil Samples Taken in July of 1972 for Greenhouse Experiment 2.

Soil No.	Farmer Names	Analyses					
		Lb / Ac			S* Level	pH	O.M.
		N	P	K			
A - 1	Breton 4	10	35	355	L+	6.6	L
A - 2	Breton 5	11	28	300	L-	6.7	L
A - 3	Hicox	6	46	600	M-	5.9	M
A - 4	Tovell	1	22	750	L	6.1	M-
A - 5	Woodward	8	39	1,000	L+	6.6	M-

* L- = 0.0 - 1.0 ppm S
 L = 1.1 - 2.0 ppm S
 L+ = 2.1 - 3.0 ppm S
 M- = 3.1 - 5.0 ppm S

Table I. Moisture and Weight Data for Soils of Greenhouse
Experiment 2

Soil No.	Farmer's Name	Soil Weight g/pot	Hygroscopic Moisture, %	Water Content at F.C., %
A - 1	Breton 4	2,850	2.2	19
A - 2	Breton 5	2,700	2.4	18
A - 3	Hicox	2,300	4.2	30
A - 4	Tovell	2,200	7.5	37
A - 5	Woodward	2,400	3.9	38

Table J. Ca and Mg Content of Barley, 1971 Field Experiments

Site No.	% Ca						% Mg					
	Straw			Grain			Straw			Grain		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
1	0.20	0.32	0.30	0.04	0.04	0.04	0.11	0.12	0.11	0.08	0.08	0.13
2	--	--	--	0.02	0.04	0.05	--	--	--	0.09	0.08	0.08
3	0.29	0.48	0.50	0.04	0.05	0.05	0.08	0.09	0.09	0.08	0.08	0.08
4	0.30	0.38	0.33	0.03	0.03	0.03	0.19	0.19	0.15	0.10	0.06	0.08
5	0.58	0.35	0.45	0.04	0.04	0.04	0.15	0.09	0.08	0.10	0.08	0.06
6	0.28	0.25	0.21	0.03	0.04	0.03	0.18	0.10	0.11	0.13	0.09	0.09
7	0.34	0.39	0.41	0.03	0.05	0.05	0.12	0.11	0.11	0.08	0.06	0.08

Table K. Ca and Mg Content of Rape, 1971 Field Experiments

Site No.	% Ca						% Mg					
	Straw			Seed			Straw			Seed		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
1	0.92	0.82	0.79	0.30	0.35	0.36	0.20	0.18	0.18	0.33	0.33	0.33
2	0.90	0.81	0.60	0.30	0.24	0.44	0.14	0.20	0.14	0.31	0.33	0.31
3	1.16	1.16	1.15	0.44	0.57	0.46	0.13	0.13	0.11	0.29	0.33	0.30
4	0.78	0.84	0.84	0.30	0.44	0.34	0.29	0.33	0.30	0.33	0.33	0.33
5	0.89	0.78	1.02	0.21	0.46	0.46	0.09	0.06	0.10	0.31	0.31	0.31
6	0.80	0.95	0.70	0.34	0.27	0.25	0.21	0.24	0.18	0.33	0.33	0.33
7	0.71	0.99	0.81	0.40	0.42	0.45	0.11	0.17	0.15	0.31	0.30	0.29

Table L. Ca and Mg Content of Alfalfa, 1971 Field Experiments

Site No.	% Ca			% Mg		
	Nil	NPK	NPKS	Nil	NPK	NPKS
1	1.25	1.57	1.69	0.20	0.26	0.27
2	1.42	1.22	1.11	0.21	0.22	0.18
3	1.18	1.53	1.26	0.13	0.16	0.14
4	1.44	1.29	1.15	0.24	0.22	0.20
5	1.44	1.22	1.10	0.15	0.14	0.13
6	0.98	1.08	1.10	0.18	0.20	0.20
7	1.66	1.36	1.27	0.25	0.21	0.22

Table M. Ca Content of Barley, in percent, Greenhouse Experiment 1

Soil No.	Second Cut Straw*			Mature Straw			Grain		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
<u>Low S</u>									
2	0.27	0.63	0.63	0.74	0.78	0.74	0.03	--	0.03
4	0.32	0.42	0.28	0.53	0.55	0.57	0.03	--	0.04
6	0.54	1.15	0.53	0.60	0.89	0.60	0.02	--	0.03
9	0.53	0.50	0.43	0.54	0.63	0.50	0.03	--	0.03
12	0.37	1.20	0.53	0.41	0.97	0.58	0.02	--	0.02
<u>Medium-High S</u>									
10	0.33	0.68	0.72	0.50	0.98	0.75	0.03	0.03	0.03
13	0.26	0.53	0.53	0.47	0.64	0.77	0.02	0.02	0.03
16	0.36	0.21	0.23	0.39	0.38	0.42	0.02	--	0.03
20	0.31	0.90	0.35	0.51	0.92	0.96	0.02	0.03	0.04

* 60 days after seeding.

Table N. Mg Content of Barley, in percent, Greenhouse Experiment 1

Soil No.	Second Cut Straw*			Mature Straw			Grain		
	Nil	NPK	NPKS	Nil	NPK	NPKS	Nil	NPK	NPKS
<u>Low S</u>									
2	0.17	0.36	0.28	0.37	0.30	0.27	0.14	--	0.10
4	0.19	0.17	0.11	0.36	0.22	0.18	0.13	--	0.11
6	0.33	0.34	0.19	0.33	0.26	0.19	0.09	--	0.10
9	0.38	0.35	0.19	0.31	0.30	0.22	0.16	--	0.11
12	0.31	0.34	0.25	0.20	0.26	0.16	0.12	--	0.08
<u>Medium High S</u>									
10	0.14	0.19	0.33	0.18	0.25	0.19	0.12	0.08	0.09
13	0.14	0.41	0.33	0.25	0.29	0.31	0.10	0.10	0.10
16	0.28	0.10	0.11	0.25	0.12	0.14	0.14	--	0.13
20	0.13	0.31	0.13	0.24	0.32	0.31	0.12	0.15	0.12

* 60 days after seeding.

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